

TITLE

METHOD FOR DEPOSITING GALLIUM OXIDE COATINGS
ON FLAT GLASS

BACKGROUND OF THE INVENTION

10 1. Field of the Invention

This invention relates to a process for depositing gallium oxide coatings on a flat glass substrate.. More particularly, this invention relates to an atmospheric chemical vapor deposition process for producing gallium oxide coatings at high growth rates on flat glass using a coating precursor gas mixture comprising a gallium halide and an 15 organicester.

2. Summary of Related Art

Gallium oxide coatings have been used, primarily, in connection with the production of semiconductor materials, for example, as a passivation layer for GaAs semiconductor wafers. It has also been formed by various methods on glass for uses in 20 luminescent phosphor, solar cell, and deep-ultraviolet transparent conducting oxide applications.

An article entitled "Synthesis of Homoleptic Gallium Alkoxide Complexes and the Chemical Vapor Deposition of Gallium Oxide Films", M. Valet and D.M. Hoffman, Chem Mater, 2001, 13, 2135-2143, describes the use of low pressure chemical vapor deposition using organo-gallium and O₂ precursors to form Ga₂O₃ films at substrate temperatures of 300-700° C. Deposition rates were reported to be less than 50Å /min, i.e., less than 0.83Å/sec.

Other investigations utilizing low pressure chemical vapor deposition have reported forming gallium oxide films, but also at a quite low deposition rates.

30 Examples include:

Battiston et al. Thin Solid Films, 1996, 279, 115 (Growth rates of

5 117Å/min i.e., 1.95Å/sec.)

- Ballarin et al. Inorg. Chim. Acta, 1994, 217, 71 (Growth rates not reported)
- Minea et al. J. Mater. Chem. 1999, 9, 929. (Growth rates less than 3800Å/min i.e., less than 63.3Å/sec.)

10 Gallium oxide thin films have also been produced using methods other than chemical vapor deposition.

U. S. Patent No. 5,451,548 utilizes electron beam evaporation of single crystal high purity $Gd_3Ga_5O_{12}$ complex compounds to form a Ga_2O_3 thin film. U.S. Patent No. 5,474,851 describes producing a gallium oxide film by reactive vapor deposition in a vacuum plus oxygen, followed by tempering. U. S. Patent No. 5,897,812 describes producing oxide/phosphors based on doped gallium oxides using RF magnetron sputtering for electroluminescent display materials.

15 It would be desirable to form gallium oxide films at essentially atmospheric pressure and to produce them at deposition rates compatible with time-critical manufacturing processes, for example, production of flat glass by the well-known float method. Those skilled in the art have continued to search for a method of producing gallium oxide films meeting the above-noted criteria in order to have available, affordable films for optical thin film stack designs.

25 SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a chemical vapor deposition process for laying down a gallium oxide coating on a hot glass substrate using a precursor gas mixture containing an inorganic gallium halide, an organic ester, and optionally including molecular oxygen.

30 Preferably, the present invention provides a process for depositing a gallium oxide coating on hot glass substrate comprising the steps of:

5 (a) preparing a precursor gas mixture containing an inorganic gallium halide and an organic ester for formation of gallium oxide,

(b) maintaining said precursor gas mixture at a temperature below the temperature at which the gallium halide reacts to form the gallium oxide while delivering the mixture to a coating chamber opening onto the hot glass,

10 (c) introducing the precursor gas mixture into the coating chamber whereby the mixture is heated to cause deposition of the gallium oxide, by incorporating oxygen from the organic ester onto the hot glass surface.

15 BRIEF DESCRIPTION OF THE DRAWINGS

The above, as well as other advantages of the present invention, will become readily apparent to those skilled in the art from the following detailed description of preferred embodiments when considered in the light of the accompanying drawings in which:

20 Fig. 1 is a schematic view of a vertical section of an apparatus for practicing a float glass process which includes gas distributors suitably positioned to enable the practicing of the method of the present invention.

~~Fig. 2 is broken sectional view of an article coated according to this invention.~~

Fig. 3 is an enlarged schematic end view of a gas distributor beam suitable for use in practicing the present invention.

~~Fig. 4 is an enlarged schematic end view of an alternative gas distributor beam which may be used in practicing the present invention.~~

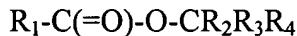
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DESCRIPTION OF THE PREFERRED EMBODIMENT

It has been found that organic esters may be used as the source of oxygen, in combination with inorganic gallium halides to form gallium oxide coatings without requiring the presence of water vapor or gaseous oxygen, however, molecular oxygen may be used with some esters. Such organic esters containing 3-18 carbon atoms may 10 be used with the invention, however, it is preferred to use organic esters containing from three to six carbon atoms, since larger molecules tend to be less volatile and hence less convenient for use in the CVD process of the present invention.

Esters useful as precursor materials in connection with the present invention can be described by the following formula:

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where R_1-R_3 are H, or a short chain, saturated organic group having 1 to 4 carbon atoms and R_4 is a short chain, saturated organic group having 1 to 4 carbon atoms.

Preferred esters for use as sources of oxygen in the practice of the present invention include, ethyl acetate, isobutyl acetate, n-butyl acetate and t-butyl acetate and 20 ethyl formate. A particularly preferred organic source of oxygen is ethyl acetate.

The method of the present invention is generally practiced in connection with the formation of a continuous glass ribbon substrate, for example during a float glass production process. However, the method of the present invention may be employed in coating flat glass substrates in spray pyrolysis CVD coating systems.

25

While it is contemplated that the precursors could be combined at, or very near, the surface of the glass, the present invention involves the preparation of a precursor gas mixture which includes gallium chloride, particularly gallium trichloride ($GaCl_3$) and an organic ester ; a carrier gas or diluent, for example, nitrogen, air or helium, will normally also be included in the gas mixture. Since thermal decomposition of the 30 organic ester may initiate the gallium oxide deposition reaction at a high rate, it is desirable that the precursor mixture be kept at a temperature below the thermal

5 decomposition temperature of the organic ester to prevent prereaction of the gaseous mixture resulting in formation of the gallium oxide.

The gaseous mixture is maintained at a temperature below that at which it reacts to form the gallium oxide, and is delivered to a location near a flat glass substrate to be coated, the substrate being at a temperature above the reaction temperature (and above 10 the decomposition temperature of the organic ester in the precursor gas mixture).

The precursor gas mixture is thereafter introduced into the vapor space directly over the substrate. The heat from the substrate raises the temperature of the precursor gas above the thermal decomposition temperature of the organic oxygen compound. The organic ester then decomposes and by reaction with the gallium chloride, produces 15 a gallium oxide coating on the substrate.

While the exact role of the organic ester in the deposition of gallium oxides from gallium trichloride has not been established, one plausible mechanism is as follows:

1. The ester undergoes an intra-molecular gas phase pyrolytic elimination to give the 20 corresponding carboxylic acid and an olefin
2. The carboxylic acid produced in step 1 dehydrates intra-molecularly, via further pyrolysis, to provide water and a ketene
- 25 3. The water generated in step 2 then reacts with gallium chloride to give gallium oxide via hydrolysis

If the organic ester first reacts with gallium trichloride to give a Lewis acid-base complex, it does not necessarily preclude the proposed mechanism (steps 1-3) from 30 taking place.

The present invention permits the production of gallium oxide coatings deposited on hot glass at a high deposition rate, preferably over 75Å/second and more preferably over 100Å/sec.

High deposition rates are important when coating substrates in a manufacturing

5 process. This is particularly true for an on-line float glass process where the glass
ribbon is traveling at a specific line speed and where a specific coating thickness is
required. The deposition rates obtained with the preferred embodiments of the present
invention may be two times higher than the deposition rate with other known methods
for depositing gallium oxide coatings. Especially high deposition rates for gallium
10 oxide may be achieved with the present invention using a precursor mixture including
an ester having 3-6 carbon atoms.

The deposition rate is dependent upon the particular organic ester used, and the
concentrations of both the organic ester and the gallium chloride, as well as the
temperature of the glass. For any particular combination of compounds, the optimum
15 concentrations (and in particular the optimum proportion of the organic ester to gallium
chloride) and flow rates for rapid coating deposition may be determined by simple trial.
However, it will be appreciated that the use of higher concentrations of reactants and
high gas flow rates is likely to result in a less efficient overall conversion of the
reactants into a coating, so that the optimum condition for commercial operation may
20 differ from the conditions which provide the highest deposition rates.

The method of the invention permits the production, at high rates, of gallium
oxide coatings on hot flat glass substrates on line during the glass production process.
The gallium oxide coatings produced by the inventive method have been found to have
intermediate refractive indices in the range of 1.7-1.95, permitting the achievement of
25 desired optical effects, especially when used in combination with other coating layers.
The gallium oxide coatings may be doped, for example with fluorine, to alter the optical
constants of the coating.

~~Referring now more particularly to the drawings, there is illustrated generally at~~
10 ~~in Fig. 1~~ [[a]] A float glass installation may be utilized as a means for practicing the
30 method of the present invention. The float glass apparatus more particularly comprises
a canal section [[12]] along which molten glass [[14]] is delivered from a melting

5 furnace (~~not shown~~), to a float bath section [[16]] wherein a continuous glass ribbon
[[18]] is formed in accordance with the well known float process. The glass ribbon
[[18]] advances from the bath section [[16]] through an adjacent annealing lehr [[20]]
and a cooling section [[22]]. The continuous glass ribbon [[18]] serves as the substrate
upon which the gallium oxide coating is deposited in accordance with the present
10 invention.

15 The float section [[16]] includes a bottom section [[24]] within which a bath of
molten tin [[26]] is contained, a roof [[28]], opposite sidewalls [[30]], and end walls
[[32]]. The roof [[28]], side walls [[30]], and end walls [[32]] together define an
enclosure [[34]] in which a non-oxidizing atmosphere is maintained to prevent
15 oxidation of the molten tin.

20 Additionally, gas distributor beams ~~64, 66 and 68~~ are located in the bath section
[[16]]. The gas distributor beams ~~64 and 66~~ in the bath section may be employed to
apply additional coatings onto the substrate prior to applying the gallium oxide coating
by the method of the present invention. The additional coatings may include silicon and
20 silica.

25 In operation, the molten glass [[14]] flows along the canal [[36]] beneath a
regulating tweel [[38]] and downwardly onto the surface of the tin bath [[26]] in
controlled amounts. On the tin bath the molten glass spreads laterally under the
influences of gravity and surface tension, as well as certain mechanical influences, and it
25 is advanced across the bath to form the ribbon [[18]]. The ribbon is removed over lift
out rolls [[40]] and is thereafter conveyed through the annealing lehr [[20]] and the
cooling section [[22]] on aligned rolls [[42]]. The application of the coating of the
present invention may take place in the float bath section [[16]], or further along the
production line, for example in the gap between the float bath and the annealing lehr, or
30 in the annealing lehr.

35 A suitable non-oxidizing atmosphere, generally nitrogen or a mixture of nitrogen

5 and hydrogen in which nitrogen predominates, is maintained in the bath enclosure [[34]] to prevent oxidation of the tin bath. The atmosphere gas is admitted through conduits [[44]] operably coupled to a distribution manifold [[46]]. The non-oxidizing gas is introduced at a rate sufficient to compensate for normal losses and maintain a slight positive pressure, on the order of about 0.001 to about 0.01 atmosphere above ambient
10 atmospheric pressure, so as to prevent infiltration of outside atmosphere. For purposes of the present invention the above-noted pressure range is considered to constitute normal atmospheric pressure. Heat for maintaining the desired temperature regime in the tin bath [[26]] and the enclosure [[34]] is provided by radiant heaters [[48]] within the enclosure. The atmosphere within the lehr [[20]] is typically atmospheric air, as the
15 cooling section [[22]] is not enclosed and the glass ribbon is open to the ambient atmosphere. Ambient air may be directed against the glass ribbon as by fans [[50]] in the cooling section. Heaters (~~not shown~~) may also be provided within the annealing lehr for causing the temperature of the glass ribbon to be gradually reduced in accordance with a predetermined regime as it is conveyed therethrough.

20 ~~Fig. 1 illustrates the use of gas~~ Gas distributor beams 64, 66 and 68 are, generally, positioned in the float bath [[16]] to deposit the various coatings on the glass ribbon substrate. The gas distributor beam is one form of reactor that can be employed in practicing the process of the present invention.

25 A conventional configuration for the distributor beams suitable for supplying the precursor materials in accordance with the invention is, [[shown]] generally, schematically at Fig. 3. A ~~an~~ inverted generally channel-shaped framework [[70]] formed by spaced inner and outer walls [[72]] and [[74]] defining at least two [defines] enclosed cavities ~~76 and 78~~. A suitable heat exchange medium is circulated through the enclosed cavities [[76, 78]] in order to maintain the distributor beams at a desired
30 temperature.

The precursor gas mixture is supplied through a fluid cooled supply conduit

5 [80]]. The supply conduit [[80]] extends along the distributor beam and admits the gas through drop lines [[82]] spaced along the supply conduit. The supply conduit [[80]] leads to a delivery chamber[[84]] within a header [[86]] carried by the framework.
10 Precursor gases admitted through the drop lines [[82]] are discharged from the delivery chamber [[84]] through a passageway [[88]] toward a coating chamber defining a vapor space opening onto the glass where they flow along the surface of the glass ~~18 in the direction of the arrows in Fig. 3.~~

15 Baffle plates [[90]] may be provided within the delivery chamber [[84]] for equalizing the flow of precursor materials across the distributor beam to assure that the materials are discharged against the glass [[18]] in a smooth, laminar, uniform flow entirely across the distributor beam. Spent precursor materials are collected and removed through exhaust chambers [[92]] along the sides of the distributor beam.

Various forms of distributor beams used for chemical vapor deposition are suitable for the present method and are known in the prior art.

20 One such alternative distributor beam configuration is illustrated schematically in Fig. 4 of the drawings. ~~Using this distributor, which is generally designated 100, the precursor gas mixture is introduced generally into the precursor gas mixture~~ through a gas supply duct [[101]] where it is cooled by cooling fluid circulated through cooling ducts 102 and 103. Gas supply duct [[101]] opens through an elongated aperture [[104]] into a gas flow restrictor[[105]].

25 [[Gas]] The gas flow restrictor [[105]] comprises a plurality of metal strips longitudinally crimped in the form of a sine wave and vertically mounted in abutting relationship with one another extending along the length of the distributor. Adjacent crimped metal strips are arranged "out of phase" to define a plurality of vertical channels between them. These vertical channels are of small cross-sectional area relative to the 30 cross-sectional area of the gas supply duct[[101]], so that the gas is released from the gas flow restrictor [[105]] at substantially constant pressure along the length of the

5 distributor.

The coating gas is released from the gas flow restrictor into the inlet side [[107]] of a substantially U-shaped guide channel generally designated 106 comprising an inlet leg[[107]], a coating chamber[[108]] which opens onto the hot glass substrate [[110]] to be coated, and an exhaust leg[[109]], whereby used coating gas is withdrawn from 10 the glass. The rounded corners of the blocks defining the coating channel promote a uniform laminar flow of coating parallel to the glass surface across the glass surface to be coated.

The following examples (in which gas volumes are expressed under standard conditions, i.e. one atmosphere pressure and ambient temperature, unless otherwise 15 stated) which constitute the best mode presently contemplated by the inventors for practicing the invention, are presented solely for the purpose of further illustrating and disclosing the present invention, and are not to be construed as a limitation on, the invention:

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EXAMPLES

Example 1

The following experimental conditions are applicable to Example 1-3.

A laboratory furnace having a moving conveyor to move a glass sheet, or sheets, through said furnace at a rate of 125-150 inches/minute (ipm), also contains a single, 25 10-inch wide, bi-directional coater, the coater being suitable for conveying vaporized reactants to the surface of the glass sheets in order to form a film or film stack by chemical vapor deposition.

The glass sheets are heated to approximately 1170°F, while the coater, at the reactor face, i.e., the portion nearest the glass surface is at a temperature of 30 approximately 500°F.

Total gas flow was essentially 32 standard liters per minute (slm).

5 Preparation of the various precursor materials is accomplished by utilizing multiple source chambers known as "bubblers", there being one for each of ethyl acetate (EtOAc) and gallium trichloride (GaCl₃) which are maintained at specific temperatures. Helium gas is introduced into the bubbler, at a particular flow rate.

10 Table 1 summarizes the deposition conditions and the resulting film thickness for the examples. Film thickness was determined optically.

Table 1.

Example	% GaCl ₃	% EtOAc	% O ₂	% HF	Thickness (Å)	Line speed (ipm)	Growth rate (Å/s)
1	1.5	5	0	0	392	125	82
2	2	10	22	0	538	150	135
3	2	10	22	1.3	456	150	114

15 As can be seen from the data of Table 1, acceptable deposition rates may be achieved utilizing the method of the present invention using only gallium trichloride and ethyl acetate (Example 1). Examples 2 and 3 show even higher deposition rates with the inclusion of molecular oxygen alone, and molecular oxygen in combination with hydrofluoric acid added to gallium trichloride and ethyl acetate. These deposition rates were achieved even though the line speed of the substrate for Examples 2 and 3
20 was increased over that for Example 1.

The various reactants described above are combined in the coater to deposit a gallium oxide coating on, in this case, a clear soda-lime-silica glass sheet whereon a SiO₂ layer 200Å thick had previously been deposited.

25 Addition of molecular O₂ and/or HF to the gaseous mixture may allow one to change the optical constants of the resulting gallium oxide coating as observed in Table 2.

Table 2.

Example	% O ₂	% HF	n _{vis} (400-800 nm)	k _{vis} (400-800 nm)
1	0	0	1.748	5.69E-09
2	22	0	1.853	1.14E-06
3	22	1.3	1.903	1.67E-05

n_(vis) is the average refractive index from 400 to 800 nm. k_(vis) is the average extinction coefficient from 400 to 800 nm. (Define extinction coefficient?)

The data of Table 2 suggests that optical properties such as n_(vis) and K_(vis) may be altered or “tuned” by the addition of optional precursors, molecular oxygen and hydrofluoric acid.

The uniform, gaseous reactant mixture which is delivered to the surface of the
15 hot glass substrate in accordance with the invention preferably includes (all percentages being mole %) from about 0 to about 40 % oxygen, from about _1.5 to about 25 % organic ester, and from about _0.5 % to about 5 % gallium halide, and most preferably includes from about 10 to about 30 % oxygen, from about _3 to about 15% organic ester, and from about 1 % to about 3 % gallium halide.

It has also been noted to be preferable, when forming the gallium oxide coating in accordance with this invention, to apply a layer of a material which acts as a sodium diffusion barrier between the glass substrate and the gallium oxide coating. Coated glass articles have been found to exhibit lower haze when the gallium oxide coating deposited in accordance with the invention is applied to the glass with a sodium
25 diffusion layer therebetween, as opposed to directly on the glass. This sodium diffusion layer is preferably formed of silica. The layer of silica is preferably formed using conventional CVD techniques.

In a more preferred embodiment, a thin film of tin oxide is first deposited on the

5 surface of the hot glass substrate, with a thin film of silica deposited thereover, so that
and underlayer structure of tin oxide/silica is formed intermediate the glass and the
subsequently deposited layer of gallium oxide. In this embodiment, the silica film not
only acts as a sodium diffusion barrier but, in combination with the first (undoped) tin
oxide film, helps to suppress iridescence in the resulting coated glass article. The use of
10 such anti-iridescent layers is disclosed in U. S. Patent No. 4,377,613, which is
incorporated herein in its entirety by reference thereto.

It must be noted that the process conditions are not sharply critical for the
successful combining and delivering of vaporized reactants according to the present
invention. The process conditions described hereinabove are generally disclosed in
15 terms which are conventional to the practice of this invention. Occasionally, however,
the process conditions as described may not be precisely applicable for each compound
included within the disclosed scope. Those compounds for which this occurs will be
readily recognizable by those ordinarily skilled in the art. In all such cases, either the
process may be successfully performed by conventional modifications known to those
20 ordinarily skilled in the art, e.g., by increasing or decreasing temperature conditions, by
varying rates of combination of the reactants, by routine modifications of the
vaporization process conditions, etc., or other process conditions which are otherwise
conventional will be applicable to the practice of the invention.

It will also be noted that the process of the invention may be repeated as desired
25 on a given substrate so as to form a coating consisting of several successive layers, the
composition of each layer not necessarily being identical. It is, of course, obvious that
for a given flow rate of the reactants, the thickness of a coating layer depends on the rate
of movement of the substrate. Under these conditions, the reaction stations may, if
desired, be multiplied by juxtaposing two or more coating devices. In this way,
30 successive layers are superimposed before the layers have had time to cool, producing a
particularly homogeneous overall coating.

5 The invention has been disclosed in what is considered to be its preferred embodiment. It must be understood, however, the specific embodiments are provided only for the purpose of illustration, and that the invention may be practiced otherwise than as specifically illustrated without departing from its spirit and scope.

5 WHAT IS CLAIMED IS:

1. A chemical vapor deposition process for deposition of a gallium oxide coating on a hot glass substrate comprising:

10 preparing a precursor gas mixture containing an inorganic gallium halide and an organic ester for formation of gallium oxide;

 maintaining the precursor gas mixture at a temperature below the temperature at which the gallium halide reacts to form the gallium oxide while delivering the mixture to a coating chamber opening onto the hot glass; and

15 introducing the precursor gas mixture into the coating chamber, whereby the mixture is heated to cause deposition of the gallium oxide incorporating oxygen from the organic source, onto the hot glass surface.

2. The process for depositing the gallium oxide on the substrate as recited in claim 1, wherein the organic ester is of the form

20 $R_1-C(=O)-O-CR_2R_3R_4$

 wherein R_1-R_3 are H or a short-chain saturated organic group having 1 to 4 carbon atoms and R_4 is a short-chain, saturated organic group having 1 to 4 carbon atoms.

25 3. The process for depositing the gallium oxide coating on the substrate as recited in claim 1, wherein the organic ester is selected from the group consisting of: ethyl acetate, isobutyl acetate, n-butyl acetate, and t-butyl acetate and ethyl formate.

30 4. The process for depositing the gallium oxide coating on the substrate as recited in claim 1, wherein the substrate is a float glass ribbon.

5 5. The process for depositing the gallium oxide coating on the substrate as
recited in claim 1 wherein the inorganic gallium halide is gallium trichloride.

10 6. The process for depositing the gallium oxide coating as recited in claim 1
wherein the gallium oxide is deposited onto the hot glass at a deposition rate greater
than or equal to 75Å/sec.

15 7. The process for depositing the gallium oxide coating as recited in claim 6,
wherein the gallium oxide is deposited onto the hot glass at a deposition rate greater
than or equal to 100Å/sec.

20 8. The process for depositing the gallium oxide coating on hot flat glass as
recited in claim 4, wherein the precursor gas mixture flows over the float glass ribbon to
be coated under laminar flow conditions.

25 9. The process for depositing the gallium oxide coating on the substrate as
recited in claim 4, wherein said hot glass surface is at a temperature in the range of
about 1100°-1320°F/590°C-715°C.

30 10. The process for depositing the gallium oxide coating on the glass substrate as
recited in claim 1, wherein the organic ester is ethyl acetate and said substrate is a float
glass ribbon.

35 11. The process for depositing the gallium oxide coating on the substrate as
recited in claim 1, wherein the substrate has a silica coating thereon, and the gallium
oxide coating is deposited over the silica coating.

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12. The process for depositing the gallium oxide coating on the glass substrate as recited in claim 1, wherein the gallium trichloride in the precursor gas mixture is at a concentration of about 0.5 - 5 % by volume.

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13. The process for depositing the gallium oxide coating on the glass substrate as recited in claim 12, wherein the organic ester in the precursor gas mixture is at a concentration of about 3 to 10 times the concentration of the gallium trichloride.

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14. The process for depositing the gallium oxide coating on the glass substrate as recited in claim 1, wherein said gallium oxide coating has a refractive index of about 1.7-1.95

15. A chemical vapor deposition process for depositing a gallium oxide coating on a hot glass substrate comprising:

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pre-mixing a uniform, precursor gas mixture containing an inorganic gallium halide and an organic ester having 3-6 carbon atoms;

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delivering the precursor gas mixture at a temperature below the thermal decomposition temperature of the organic ester to a location adjacent the hot glass substrate to be coated, the substrate being at a temperature above the thermal decomposition temperature of the organic ester, and the atmosphere surrounding the substrate is at, essentially, atmospheric pressure; and

30

introducing the precursor gas mixture into a vapor space above the substrate wherein the organic ester thermally decomposes, and, thereby initiates a reaction with the gallium halide to produce a gallium oxide coating on the substrate at a deposition rate greater than or equal to 100Å/sec.

16. A method of utilizing an inorganic gallium halide and an organic ester, the organic ester having 3-6 carbon atoms, to form a gallium oxide coating on a hot glass substrate by chemical vapor deposition.

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ABSTRACT OF THE DISCLOSURE

A chemical vapor deposition process for laying down a gallium oxide coating on a glass substrate through the use of an organic ester and an inorganic gallium halide. The organic ester preferably contains 3 - 6 carbon atoms which contributes to obtaining a high deposition rate. The chemical vapor deposition method to form the gallium 10 oxide coating is preferably at, essentially, atmospheric pressure. The resulting article has a gallium oxide coating which can be of substantial thickness because of the high deposition rates attainable. The coating deposition rates resulting from the method of the present invention are preferably greater than or equal to 75Å per second.